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13. ABSTRACT (Maximum 200 words)  This project developed and applied quantitative methods to determine the structure of polymers and polymer-based materials using high spation resolution electron-scattering techniques. The traditional approach to studying polymer morphology using the electron microscope has involved preferential scattering using heavy element stains. We and others have shown that such staining approaches introduce artifactual structure which interferes with the study of intrinsic polymer morphology at length scales of order 5 nm and finer. This project focused on: (i) the development and application of phase-contrast imaging via electron holography and chemical imaging via electron energy-loss spectroscopy to study the structure of polymers and polymer-based nanoparticles. The present report summarizes advances primarily in the area of chemical imaging of dry two-phase polymers. With ongoing ARO support we are currently concentrating on the development and application of EELS-based methods to map water and other solvents in frozen-polymers and organic materials using chemical imaging combined with cryomicroscopy.				
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**FINAL REPORT: 8/1/00 - 12/31/03**

**ARMY RESEARCH OFFICE GRANT DAAD19-00-1-0481**

**QUANTITATIVE HIGH RESOLUTION  
ELECTRON SCATTERING  
FROM POLYMERS**

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## **OVERVIEW AND GOAL**

This research project continued ARO-supported work on the development/application of electron scattering methods in the TEM to quantitatively measure polymer morphology. This particular project focused on problems demanding nanometer-scale spatial resolution where staining methods are not useful. The research concentrated on phase-contrast imaging based on transmission electron holography and chemical imaging based on spatially resolved electron energy-loss spectroscopy.

The work addressed three major hypotheses:

Hypothesis i: Phase-contrast imaging can be used to determine the morphology of unstained two-phase polymers.

Hypothesis ii: Model geometries, principally spherical ones, can be used to quantitatively determine fundamental properties of electron-specimen interaction such as mean inner potential and inelastic electron scattering cross sections.

Hypothesis iii: Quantitative electron-scattering data can be exploited to establish morphological properties (e.g. size, shape, phase distribution, nature of internal interfaces, and self-assembly behavior) in mesoscopic globular polymers.

## **RESULTS**

### **Highlights:**

1. We successfully demonstrated that all three hypotheses are true.
2. Five students and one post-doctoral research associate were partially or fully supported and trained under this grant. Of these, three have left Stevens, two of whom work for a United-States technology company and the third is a post-doctoral scientist at Cambridge University.
3. PI Libera presented 12 different invited seminars during the course of the project, one of which was at the 15th International Congress on Electron Microscopy in Durban, South Africa.
4. 10 papers were published in archival journals.
5. One patent application was submitted to the US Patent Office.
6. This project has led us to the point of now combining the EELS-mapping method with cryo-TEM to study hydrated and solvated polymers. This is the subject of our current ARO grant which started 8/1/03.

## **PRESENTATIONS** (\*\* invited)

\*\*American Chemical Society, Boston, 8/02.

\*\*NJCBM Tissue Engineering Seminar Series, Rutgers University, 4/9/02

\*\*AIMS Symposium, NJIT, 5/8/02

\*\*Third International Symposium on Adhesion Aspects of Polymer Coatings, Providence, RI 5/22/02.

\*\*Montana State University, 7/17/02

\*\*XVth International Congress on Electron Microscopy, Durban, South Africa, September, 2002.

\*\* Dow Chemical Corporation, 4/19/01

\*\* Dow Corning Corporation, 4/20/01

\*\* University of Wisconsin, 3/9/01

\*\* Rutgers University, 2/13/01

\*\* IBM Research Division, 6/22/01

\*\* Army Research Laboratory, 8/16/01

*Spatially Resolved Electron Energy Loss Measurements Of Fast Secondary Electron Range In Thin Polymer Films*, Materials Research Society Meeting, Boston MA, December 2000.

*Phase Separation In Poly(Pseudo Amino Acid) – PEG Blends And Copolymers*, Materials Research Society Meeting, Boston MA, December 2000.

*Epoxy Infiltration Into Nanoporous Aluminum Oxide*, Materials Research Society Meeting, Boston MA, December 2000.

## **PERSONNEL SUPPORTED**

1) Dr. Jennifer Taylor, Partially supported doctoral student on the development and application of spatially-resolved electron diffraction methods to determine the structure of LCP fibers (Ph.D. 5/01). Currently working as a post-doctoral research scientist within the Medical Materials group at Cambridge University (UK).

2) Dr. Alex Chou: partially supported second-generation doctoral student on holography and phase contrast imaging of mesoscopic polymer nanoparticles (Ph.D. granted 12/13/01). Currently working as an Electron Optics Engineer at Emispec Systems (Tempe, AZ).

3) Dr. Aziz Aitouchen, partially supported post-doctoral research scientist concentrating on the development and application of spatially resolved electron energy loss spectroscopy. Principal support from Unilever Research. Currently working at Emispec systems (Tempe, AZ).

4) Mr. Alioscka Sousa, fully supported doctoral student on the development and application of spatially-resolved electron energy-loss spectroscopy and its application to mapping nano/meso scale morphology in unstained multiphase dry and hydrated polymers (Ph.D. anticipated 5/05).

5) Mr. Peter Krsko, partially supported doctoral student studying e-beam patterning of polymer thin films. (Ph.D. anticipated 5/05).

6) Mr. Merih Sengonul, partially supported doctoral student developing surface-modified protein-based nanocontainers as high-value-added polymer additives and studying the morphology of nanocontainer/polymer blends using TEM. (Ph.D. anticipated 5/04).

## **AWARDS**

Prof. Matthew Libera was awarded the degree of Master of Engineering Honoris Causa from the Stevens Institute of Technology, Sept. 2003.

Mr. Peter Krsko – received a Microscopy Society of America Presidential Scholar Award which was presented at the August 2002 MSA meeting in Quebec.

Dr. Jennifer Taylor – received the Stevens Morton Traum Award for Outstanding Doctoral Research May 2001.

Mr. Peter Krsko – received a Microscopy Society of America award for undergraduate research 2001.

## **INVENTIONS**

Patent disclosure submitted to Stevens and filed as a provisional patent application entitled *Patterned Polymer Microgel*. Submitted to the United States Patent Office, July 2003.

## **PUBLICATIONS**

### **Published Archival Papers**

1. Chou, T.M. and M. Libera, *Mean free paths for inelastic electron scattering in silicon and poly(styrene) nanospheres*. Ultramicroscopy, 2003. **94**(1): p. 31-35.
2. Chou, T.M., M. Libera, and M. Gauthier, *Quantitative phase contrast imaging of arborescent graft polystyrene by off-axis transmission electron holography*. Polymer, 2003. **44**(10): p. 3037-3043.
3. Krsko, P., M. Mansfield, S. Sukhishvili, R. Clancy, and M. Libera, *Electron-Beam Patterned Poly(Ethylene Glycol) Microhydrogels*. Langmuir, 2003. **19**: p. 5618-5625.
4. Taylor, J., A. Romo-Uribe, and M. Libera, *Molecular orientation gradients in thermotropic liquid crystalline polymers*. Polymers for Advanced Technologies, 2003. **14**(9): p. 595-600.
5. Chou, T.M., P. Prayoonthong, A. Aitouchen, and M. Libera, *Nanoscale artifacts in RuO<sub>4</sub>-stained poly(styrene)*. Polymer, 2002. **43**(7): p. 2085-2088.
6. Douglas, T., E. Strable, et al., *Protein Engineering of a Viral Cage for Constrained Nano-Materials Synthesis*. Advanced Materials, 2002. **14**(6): p. 415-418.
7. Taylor, J., A. Romo-Uribe, and M. Libera, *Bimodal orientation defects in main-chain thermotropic liquid crystalline polymer fibers*. Macromolecules, 2002. **35**(5): p. 1751-1756.
8. Taylor, J., A. Romo-Uribe, and M. Libera, *Spatially resolved electron diffraction and the determination of orientational order parameters in thermotropic liquid crystalline polymer*. Polymer, 2002. **43**(ER5): p. 1641-1648.
9. Arayasantiparb, D., S. McKnight, and M. Libera, *Epoxy Infiltration into Nanoporous Aluminum Oxide*. Journal of Adhesion, 2001. **76**(4): p. 353.
10. Arayasantiparb, D., S. McKnight, and M.R. Libera, *Compositional variation within the epoxy/adherend interphase*. Journal of Adhesion Science and Technology, 2001. **15**(12): p. 1463-1484.

### **Published Proceedings and Extended Abstracts**

1. Krsko, P., S. Sukhishvili, and M. Libera, *Surface-patterned microhydrogels*. Polymeric Materials Science and Engineering, 2003. **89**: p. 263-264.

2. Sengonul, M. and M. Libera, *Protein nanocontainer surface modification for controlled compatibility with hydrophobic polymers*. Polymeric Materials Science and Engineering, 2003. **89**: p. 302-303.
3. Aitouchen, A., S. Shi, M. Libera, and M. Misra, *Multicomponent mapping in hydrated synthetic materials by spatially resolved energy-loss spectroscopy*, in *The 15th International Congress on Electron Microscopy, Durban, South Africa*. 2002. p. 137-138.
4. Chou, T. and M. Libera, *Phase-contrast imaging of polymer nanoparticles*, in *The 15th International Congress on Electron Microscopy, Durban, South Africa*. 2002. p. 597-598.
5. Krsko, P., M. Libera, R. Clancy, and J. Kohn, *Electron-beam micropatterning of bioactive surfaces*, in *The annual meeting of the Microscopy Society of America, Quebec, Ontario*. 2002.
6. Libera, M., S. McKnight, and D. Arayasantiparb, *The width of the epoxy-alumina interphase*. Proceedings of the Annual Meeting of the Adhesion Society, 2002. **25th**: p. 482-483.
7. Libera, M., C. Trevor, and A. Aitouchen, *Dose-limited imaging and spectroscopy of polymers*, in *The 15th International Congress on Electron Microscopy, Durban, South Africa*. 2002. p. 585-586.
8. Libera, M.R., *Imaging unstained polymer morphology using energy loss spectroscopy*. Polymeric Materials Science and Engineering, 2002. **87**: p. 177.